

TRADE IN MISCELLANEOUS PRODUCTS			
ARTICLES	1914	1918	1920
Imports			
Collodion, and manufactures of, value.....	\$569,763	\$53,637	\$82,940
Explosives:			
Fulminates, gunpowder, etc., value.....	\$256,379	\$7,860,139	\$2,369,250
All other, value.....	\$600,958	\$437,010	\$765,412
Glass and glassware, value.....	\$8,191,833	\$1,723,014	\$3,582,377
Glue and glue size, lbs.....	22,714,877	2,048,543	1,410,104
Matches, value.....	\$882,812	\$3,856,961	\$1,096,982
Oilcloth for floors:			
Linoleum, sq. yds.....	3,724,086	38,584	522,999
Oilcloth, sq. yds.....	340,288	5,060	62,372
Paints, pigments, etc., value.....	\$2,325,222	\$961,047	\$1,975,769
Paper and pulp:			
Printing paper			
Not over 8 c. per lb., lbs....	536,815,288 ¹	1,203,762,118 ¹	1,322,890,825
All other, lbs.....	6,053,429	278,367	1,371,576
Surface-coated paper, lbs....	6,925,505	380,153	
Wrapping paper, lbs.....	36,515,554	6,150,942	4,983,817
Wood pulp			
Mechanical, tons.....	177,484	189,599	194,119
Chemical, unbleached, tons	302,963	296,465	442,844
Chemical, bleached, tons...	88,917	18,044	89,587
Photographic goods:			
Dry plates, value.....	(²)	\$33,857	\$25,808
Motion-picture films			
Not exposed, lin. ft.....	44,717,323 ³	47,462,715	46,485,434
Negatives, lin. ft.....	\$402,704 ⁴	\$713,363	\$1,417,774
Positives, lin. ft.....	\$20,057,144	\$3,374,497	\$3,327,566
Other films and plates, value	\$324,535	\$203,719	\$1,355,832
Soap:			
Castile, lbs.....	4,622,082	1,016,399	2,352,974
All other, value.....	\$460,485	\$211,149	\$192,103
Sugar and molasses:			
Molasses, gals.....	51,410,271	130,730,861	154,670,200
Sugar			
Beet, lbs.....	2,367,708	750	1,219,834
Cane, lbs.....	5,061,564,621	4,898,277,025	7,590,911,767
Exports			
Baking powder, lbs.....	2,725,964	6,046,455	5,595,126
Blackening and polishes, value...	\$649,395	\$1,009,100	\$2,845,110
Candles, lbs.....	3,047,756	6,761,767	7,691,420
Celluloid and manufactures, value.....	\$1,387,541	\$3,744,745	\$10,044,242
Chewing gum, value.....	\$178,630	\$1,896,135	\$2,617,483
Explosives:			
Cartridges, loaded, value....	\$3,521,533	\$13,672,371	\$9,729,937
Dynamite, lbs.....	14,464,601	18,911,668	12,566,057
Fuses, value.....	(²)	\$19,346,554	\$709,662
Gunpowder, lbs.....	989,385	340,516,883	1,721,991

¹ Valued at not above 5 cents a pound prior to April 24, 1920.² Not stated separately.³ From Oct. 3, 1913, to June 30, 1914.⁴ Stated as "All other" motion-picture films in 1914.

TRADE IN MISCELLANEOUS PRODUCTS (Concluded)			
ARTICLES	1914	1918	1920
Exports			
Explosives (Continued):			
Shells and projectiles, loaded, value.....	(¹)	\$40,130,298	\$12,295,519
All other, value.....	\$916,280	\$38,559,249	\$2,250,566
Flavoring extracts and fruit juices, value.....	(¹)	\$1,018,102	\$1,425,380
Glass and glassware, value.....	\$3,729,623	\$14,012,656	\$25,906,621
Glucose and grape sugar:			
Glucose, lbs.....	162,680,378	80,970,744	219,793,235
Grape sugar, lbs.....	36,850,496	16,887,557	25,839,015
Glue, lbs.....	2,351,770	4,935,250	13,141,294
India-rubber manufactures, value.....	\$12,441,220	\$31,675,847	\$69,226,716
Ink:			
Printers', value.....	\$443,377	\$882,062	\$1,590,096
All other, value.....	\$181,697	\$407,093	\$836,436
Matches, value.....	\$77,736	\$471,385	\$558,911
Metal polish, value.....	\$162,504	\$192,691	\$451,934
Mucilage and paste, value.....	\$95,013	\$399,295	\$654,827
Oilcloth:			
For floors, sq. yds.....	163,214	1,259,805	2,623,060
All other, value.....	\$666,479	\$1,277,777	\$2,475,699
Paints, pigments, etc.:			
Dry colors			
Carbon, bone, and lamp-black, value.....	\$421,548	\$1,111,265	\$1,959,208
All other, value.....	\$690,836	\$1,907,667	\$2,991,618
Lead			
Red, lbs.....	(¹)	4,792,330	3,027,731
White, lbs.....	16,845,154	18,235,783	34,441,918
Ready-mixed paints, gal....	852,910	1,521,588	2,553,091
Varnish, gal.....	1,069,501	736,949	1,529,592
Zinc oxide, lbs.....	29,197,790	25,862,063	30,925,983
All other, value.....	\$1,779,863	\$4,875,006	\$7,756,076
Paper and pulp:			
Newsprint, lbs.....	88,966,738	220,080,301	123,335,408
Other printing paper, lbs....	28,602,134	90,353,235	92,076,860
Wrapping paper, lbs.....	14,133,097	59,350,946	65,163,463
Writing paper and envelopes, value.....	\$1,179,232	\$4,560,084	\$7,322,859
Wood pulp, tons.....	13,481	34,805	33,972
Photographic goods:			
Motion-picture films			
Not exposed, lin. ft.....	155,359,550	57,995,064	90,398,122
Exposed, lin. ft.....	32,690,104	84,537,376	188,527,165
Other sensitized goods, value	\$1,348,216	\$2,938,756	\$4,960,928
Soap:			
Toilet or fancy, value.....	\$2,141,633	\$2,246,258	\$6,625,259
All other, lbs.....	58,547,763	82,726,757	155,891,386
Sugar and molasses:			
Molasses, gal.....	1,002,441	3,811,341	7,667,830
Sirup, gal.....	11,630,528	7,690,074	12,278,246
Sugar, refined, lbs.....	50,895,726	576,415,850	1,444,030,665
Vulcanized fiber and manufactures of, value.....	\$854,642	\$950,029	\$1,859,357
Washing powder and fluids, lbs.	12,761,958	4,754,084	6,217,201

¹ Not stated separately.

ORIGINAL PAPERS

THE DIRECT SYNTHETIC AMMONIA PROCESS*

By R. S. Tour

PLANT ONE SECTION, NITRATE DIVISION, ORDNANCE DEPT., U. S. A.

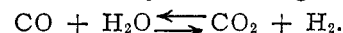
Received June 12, 1920

After much careful experimental work,¹ Prof. Fritz Haber, of Karlsruhe, Germany, patented² a process whereby nitrogen and hydrogen in the presence of a reaction promoter combined directly to form ammonia, according to the equation $N_2 + 3H_2 \rightleftharpoons 2NH_3$. This is the basis of what has become known as the Haber process. The conditions necessary to bring about the combination to an appreciable extent, even in the presence of the best reaction promoters or catalysts so far developed, involve pressures of over 100 atmospheres, and temperatures over 500° C. The concentration of ammonia thus obtained in the nitrogen-hydrogen mixture, according to present practice, is of the order of 5 per cent. The catalytic synthesis is accomplished in one portion of a circulating system. The ammonia synthesized is removed continuously by liquefaction or absorption in another part of that system. The uncombined gases repeat the cycle after additional nitrogen and hydrogen have been introduced to replace that synthesized.

* Released by permission of the Chief of Ordnance.

¹ Numbers refer to References, p. 852.

The nitrogen and hydrogen necessary for the synthesis may be obtained by any of several commercial methods. For the large quantities of hydrogen necessary in commercial installations of the Haber process, the water-gas oxidation method has proved the most suitable. This involves the production of water-gas and its further reaction with an admixture of steam in the presence of a catalyst according to the equation³



The nitrogen may be obtained in the mixture by injection of air during the manufacture or oxidation of the water-gas, or by the production of a pure producer gas to be mixed with the water-gas before oxidation.^{4,5} The gas mixture after oxidation contains besides nitrogen and hydrogen large quantities of carbon dioxide, with some carbon monoxide. Extensive purification is necessary,^{4,6,7} the carbon dioxide being removed by water washing at high pressures, the carbon monoxide by scrubbing with cuprous solutions, and incidental impurities by various special means. The purified gas, approximately three parts hydrogen and one part nitrogen, is then available for ammonia synthesis.

The complete process, including the manufacture of the gases, should be more properly known as the

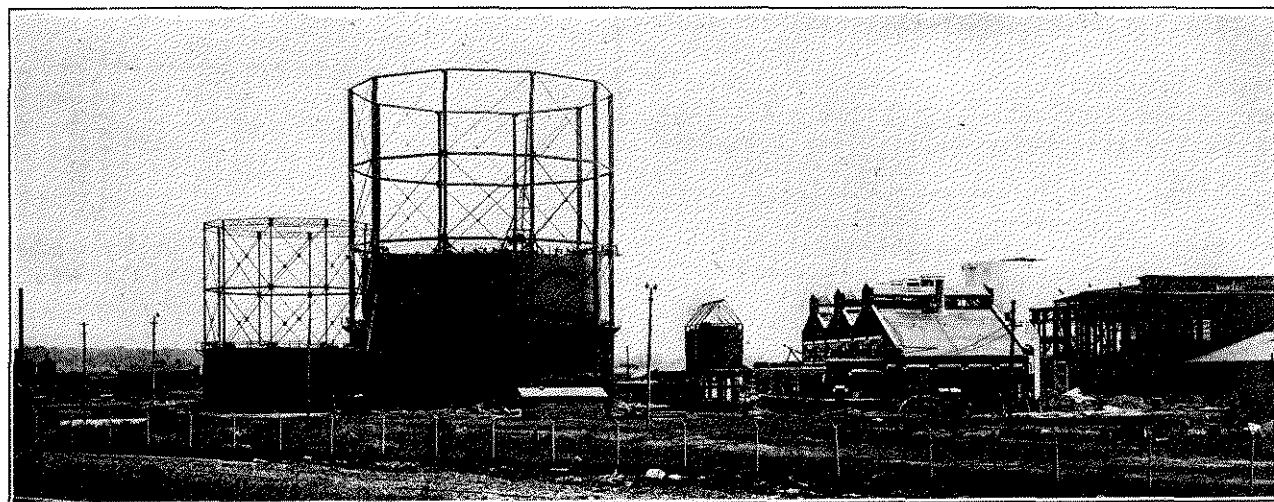


FIG. 1—GENERAL VIEW OF GAS PLANT, U. S. NITRATE PLANT No. 1

Haber-Bosch Process, crediting the development of the methods of manufacture of the pure gases to Dr. C. Bosch, of the Badische Anilin und Soda Fabrik of Ludwigshafen, Germany. A general outline of the process follows and indicates the order and the headings under which this paper will take up the various steps involved. A diagrammatic flow chart is shown in Fig. 2.

I—PRODUCTION OF RAW GASES:

Water-Gas Manufacture
 Producer-Gas Manufacture
 Mixing of Producer- and Water-Gas
 Direct Manufacture of Mixed Gas

II—OXIDATION OF CARBON MONOXIDE:

Addition of Steam before Conversion
 Heat Interchange and Catalysis
 Cooling Gas and Condensation of Excess Steam

III—PURIFICATION OF GAS:

Compression of Gas and Removal of Carbon Dioxide
 Removal of Carbon Monoxide
 Additional Purification

IV—SYNTHESIS OF AMMONIA:

Adjustment of Gas Composition
 Heat Interchange and Catalysis
 Removal of Ammonia and Circulation of Gas

I—PRODUCTION OF RAW GASES

WATER-GAS MANUFACTURE—The water-gas process with standard equipment as used in the manufacture of illuminating gas is employed to decompose steam, producing free hydrogen along with oxides of carbon. In a subsequent paragraph it is shown how the carbon monoxide is utilized for the production of more hydrogen, and how the carbon dioxide is removed. The composition of the water-gas is given in Table I. It will be noted that 100 volumes of this mixture contain approximately 50 volumes of hydrogen as such and 40 volumes of potential hydrogen (later available) in the form of carbon monoxide, making a total of 90 volumes of hydrogen.

TABLE I—WATER-GAS COMPOSITION

	Operating Ranges	
	Per cent	Per cent
CO ₂	5- 3	5- 3
CO.....	42- 45	42- 45
H ₂	51- 50	53- 52
N ₂	2	0
TOTAL, 100-100		100-100

PRODUCER-GAS MANUFACTURE—Standard methods of producer-gas manufacture may be employed to se-

cure a gas mixture rich in nitrogen. Oxides of carbon are present, and, since some steam is used with the air, hydrogen also is present. Inasmuch as this producer-gas is later added to the water-gas, the hydrogen in the former, as well as the carbon monoxide (potential hydrogen), becomes available. The producer-gas may have the composition shown in Table II. The range of composition is wide, depending on the nature of the fuel and the operating conditions. One hundred volumes of this producer-gas represents approximately 60 volumes of nitrogen and 30 volumes of hydrogen as such or potential.

TABLE II—PRODUCER-GAS COMPOSITION

	Per cent
CO ₂	5
CO.....	25
H ₂	5
CH ₄	2
N ₂	63
TOTAL, 100	

MIXING OF WATER- AND PRODUCER-GAS—To maintain the desired ratio of 3 parts of hydrogen (actual + potential) to one of nitrogen, a mixture of very nearly two volumes of water-gas to one volume of producer-gas of the above compositions would be required. The composition of the mixed gas is to a great extent independent of the compositions of the producer- and water-gases, if we assume that these gases have been mixed in proper proportion to secure the desired final ratio between the hydrogen and nitrogen. The final composition will, in normal practice, vary only within narrow limits, and should be as indicated in Table III. By solving the necessary fundamental equations the composition in the table may be deduced. One hundred volumes of this gas mixture contain about 70 volumes of actual and potential hydrogen and 23 volumes of nitrogen.

TABLE III—MIXED-GAS COMPOSITION

	Per cent
CO ₂	3- 5
CO.....	39- 36
H ₂	34- 36
N ₂	23- 22
X (CH ₄ , argon, etc.).....	1- 1
TOTAL, 100-100	

DIRECT MANUFACTURE OF MIXED GAS—In lieu of making the two gases separately and mixing them in

the desired proportions, the mixture may be made directly by the introduction of air into the water-gas machine during its "making" period.^{4,6} The net result of this direct method is the combining of the water-gas machine and the producer in one apparatus.

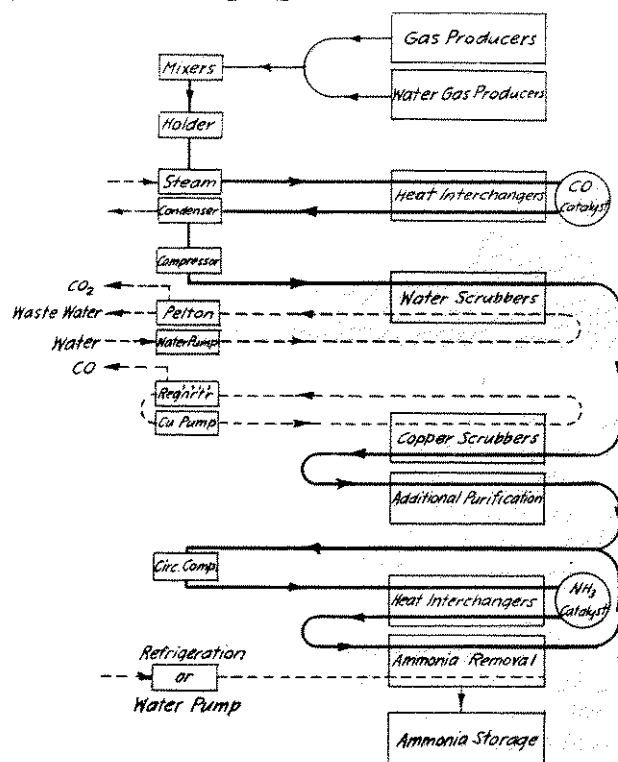
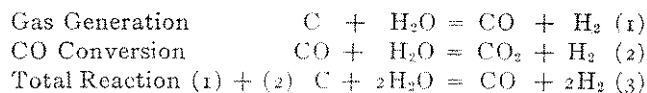


FIG. 2—DIRECT SYNTHETIC AMMONIA PROCESS FLOW CHART

A theoretical comparison leads to little choice, but operating considerations may definitely determine which of the methods to employ. Producers can use a lower grade fuel than water-gas machines, although in small plants duplication of apparatus may be the controlling factor.

II—OXIDATION OF CARBON MONOXIDE

ADDITION OF STEAM BEFORE CONVERSION—The carbon monoxide in the mixed gas will react with steam in the presence of a catalyst to produce carbon dioxide and hydrogen. This conversion is essentially a continuation of the reaction in the water-gas machine, under more favorable conditions of temperature and steam concentration.



In the first reaction, in the absence of a catalyst, high temperatures prevail, and 100 per cent excess steam is good practice. In the converter with the aid of a catalyst a lower temperature is used with a many times greater excess of steam.

It can be shown theoretically that in the CO conversion reaction the unconverted carbon monoxide concentration in equilibrium varies inversely as the proportion of steam present and directly as a function of the temperature.⁸ From Table IV it is evident that each additional volume of steam converts less additional carbon monoxide. In operation, therefore,

TABLE IV—EQUILIBRIUM PER CENT CO

Temp. ° C.	(CO + H ₂ O ⇌ CO ₂ + H ₂)		
	Inlet Steam per Volume of Inlet Gas—		
	3 Vols. Per cent	4 Vols. Per cent	5 Vols. Per cent
400	0.45	0.33	0.26
450	0.80	0.58	0.46
500	1.25	0.91	0.71
550	1.80	1.31	1.03
600	2.45	1.78	1.40
650	3.20	2.32	1.83
700	4.05	2.94	2.24

a point of diminishing net return is quickly reached, depending mainly on the relative cost of the steam as compared to the later cost of carbon monoxide removal.

HEAT INTERCHANGE AND CATALYSIS—The mixed gas containing nitrogen, hydrogen, and carbon monoxide is mixed with the necessary proportion of steam and forced through a set of heat interchangers, and on through the carbon monoxide converter wherein is a catalyst for the carbon monoxide conversion reaction. The catalysts are mainly of ferric oxide with an addition of some promoter.⁹ Such catalysts are chemically rugged against poisons, although they are physically delicate. The gas, after passing the catalyst and carrying considerable excess steam (about 90 per cent of the initial steam), passes back through the heat interchangers, giving up its heat to the incoming mixture. The heat interchanging system is important since the temperature at the catalyst must be maintained between 400° and 600° C.,^{5,9} the exact temperature depending upon the catalyst and operating conditions in general.

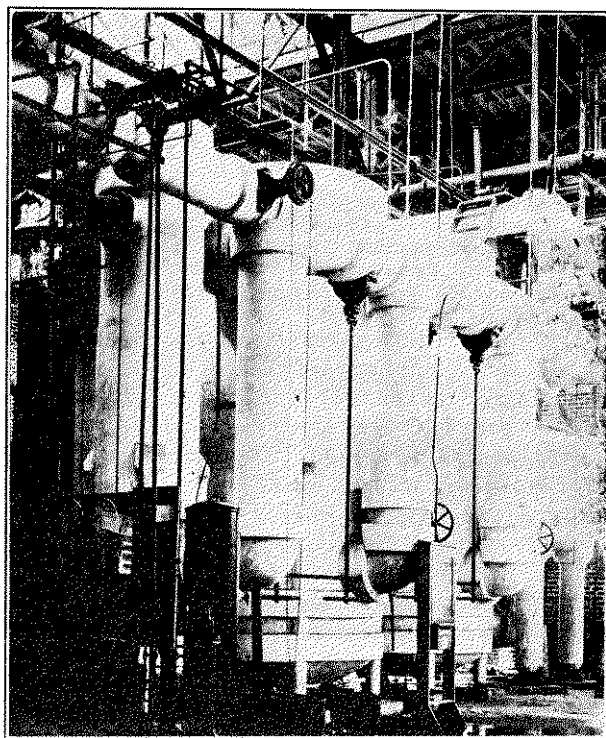


FIG. 3—CARBON MONOXIDE CONVERTER AND HEAT INTERCHANGERS

The reaction of the carbon monoxide with steam is sufficiently exothermic to produce a rise of 50° to 60° C. during catalysis. With carefully designed heat interchangers of sufficient surface, the heat of

reaction may offset radiation and heat losses, thus making the system self-maintaining in temperature. If the heat of reaction be insufficient, heat may be added by superheating the steam before admixture. However, any such external heat addition is inefficient, besides decreasing the temperature gradient across the heat interchangers. Heat may be developed more advantageously within the system by injecting air into the reacting gases, with consequent combustion either as a free flame or in the catalyst bed.⁵

If equilibrium were attained during catalysis, a gas would be secured containing but 1 to 2 per cent CO. In practice this is not reached, and 2 to 4 per cent CO remains, representing a conversion of about 90 per cent of the original carbon monoxide. Due to the conversion there is an increase of about one-third in the volume of the dry gases. The dry converted gas should have the composition shown in Table V. This analysis may also be obtained entirely by calculation.

TABLE V—GAS COMPOSITION (DRY) AFTER CONVERSION

	Per cent
CO ₂	29- 27
CO.....	2- 4
H ₂	52- 52
N ₂	17- 17
TOTAL, 100-100	
X (CH ₄ , argon, etc.).....	0.4 to 0.8

COOLING GAS AND CONDENSATION OF EXCESS STEAM—

The converted gas issues from the heat interchanger still at a somewhat elevated temperature. It is cooled and the excess steam condensed in special condensers. The composition of the gas mixture issuing from the condensers is then as given in the preceding paragraph.

III—PURIFICATION OF GAS

COMPRESSION OF GAS AND REMOVAL OF CARBON DIOXIDE—The chief impurity in the gas at this stage is carbon dioxide, which is removed by scrubbing the gas mixture with water at high pressures.^{4,6,10} The dry gas is compressed in a multi-stage compressor up to the pressure at which it is to remain through the rest of the process, or perhaps to some intermediate pressure. The optimum pressure will depend on local operating conditions. For removal of the carbon dioxide the compressed gas is passed upward in a scrubber tower, countercurrent to water flowing downward over suitable packing. The composition of the washed gas at the exit of the scrubber is given in Table VI. If desired, the residual carbon dioxide (0.1 to 1.0 per cent) remaining after water scrubbing may be removed by washing the gas with a cold caustic solution.¹¹

TABLE VI—GAS COMPOSITION AFTER WATER SCRUBBING

	Per cent
CO.....	3- 5
H ₂	73- 72
N ₂	24- 25
TOTAL, 100-100	
CO ₂	0.1 to 1.0
X (CH ₄ , argon, etc.).....	0.5 to 1.0

The following points may be of interest: The solubility of carbon dioxide increases with its partial pressure. Table VII gives cubic feet of carbon dioxide at 60° F. and 30 inches Hg dissolved in 1 cu. ft. of water. For a given CO₂ percentage in a gas the scrubbing

TABLE VII—SOLUBILITY OF CARBON DIOXIDE IN WATER¹²

CO ₂ Partial Pressure Atmos.	0° C. Vols.	12° C. Vols.
5.0	9.2	6.5
10.0	17.1	10.3
15.0	23.6	14.5
20.0	28.6	18.2
25.0	32.5	21.6
30.0	36.0	24.8

water necessary decreases with an increase of the total gas pressure. However, the energy required for pumping this decreased water at the increased pressure is not greatly altered. At a given total gas pressure, the quantity of solvent water necessary is not greatly affected by variations in CO₂ concentrations, since as the CO₂ to be dissolved decreases, the solubility also decreases. Hence, CO₂ absorption should be completed in one stage rather than in a series of stages at decreasing concentrations.



FIG. 4—DOUBLE WATER SCRUBBER TOWER SHOWING OTHER APPARATUS AND MAZE OF PIPING

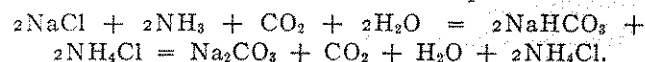
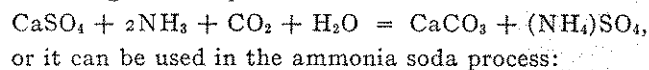
The scrubbing water with its dissolved carbon dioxide (and hydrogen sulfide), as well as some hydrogen and nitrogen, passes from the bottom of the scrubbing tower and discharges through a water wheel.^{4,6} Here the dissolved gases are liberated and much of the power

TABLE VIII—COMPOSITION OF DISSOLVED GAS RELEASED FROM SCRUBBING WATER

	Per cent
CO ₂	76- 84
H ₂	17- 11
N ₂	6- 4
X (H ₂ S, CO, etc.).....	1
TOTAL, 100-100	

used in pumping the water may be regenerated. The composition of the gas escaping from the dissolving water after pressure release will be normally as shown in Table VIII, the variation depending upon operating conditions.

The hydrogen and nitrogen dissolved represent about 10 per cent of the total of these gases being manufactured. This loss is theoretically independent of the pressure at which the scrubbing is done and is unavoidable since the solubility of hydrogen and nitrogen is not negligible. The carbon dioxide in the liberated gases is a valuable by-product. In conjunction with the ammonia synthesized, it may be used for the manufacture of ammonium sulfate by the decomposition of gypsum in the presence of ammonia, according to the equation



There are available about 45,000 cu. ft. of carbon dioxide per ton of ammonia synthesized. This is much more than is necessary to satisfy the requirements per unit of ammonia in either of the above reactions. It is not within the scope of the present paper to discuss further the various special methods¹³ of utilization of the main or by-products of the Haber process.

REMOVAL OF CARBON MONOXIDE—If an intermediate pressure has been used for water scrubbing the compression is completed and the gas passes through a scrubber similar to the water scrubber, but employing an ammoniacal cuprous solution⁷ as the dissolving medium. The spent cuprous solution coming from the bottom of the scrubber passes on, after pressure release, to a regenerating system where its carbon monoxide is removed by heat. The composition of the solution may require readjustment before it is again used.

Scrubbing the gas with the ammoniacal cuprous solution removes by reaction with the reduced copper any oxygen that may be present; removes by combination with the free ammonia the carbon dioxide residual after the water scrubbing, as well as traces of other acidic gases that may have passed through the water scrubbers; and absorbs nearly all of the 3 to 5 per cent of carbon monoxide in the gas. Table IX gives the impurities in the gas leaving the copper system.

TABLE IX—IMPURITIES IN GAS AFTER CUPROUS SCRUBBING

	Per cent
CO ₂	0
O ₂	0
CO.....	0.1–0.01
NH ₃	0.2–0.01
H ₂ O.....	0.02–less
X (CH ₄ , argon, etc.).....	1.0–0.5

Attempts have been made commercially to remove most of the carbon monoxide by a concentrated hot caustic solution^{6,14} preliminary to the cuprous scrubbing. Carbon monoxide and hot caustic soda produce directly sodium formate. Chemically the carbon monoxide removal is satisfactory, reducing the 3 to 5 per cent inlet carbon monoxide down to under 1 per cent when the optimum caustic concentration of 10 per cent¹⁵ is used at temperatures around 200° C. However, the residual carbon dioxide in the gas causes a precipitation of insoluble carbonate from the solution, and the mechanical difficulties are enormous. The consumption of caustic under operating con-

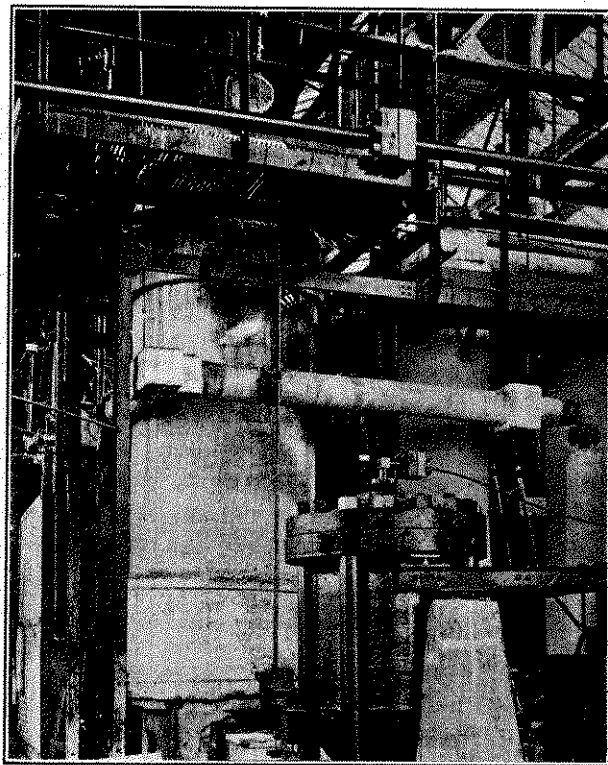


FIG. 5—AMMONIA CATALYST BOMB WITH HEAT INTERCHANGERS ON THE RIGHT

ditions is prohibitive unless improved methods of recovery are developed.

ADDITIONAL PURIFICATION—After the cuprous scrubbing, further purification may be necessary depending on the sensitiveness of the catalyst used for the ammonia synthesis. This purification may consist of refrigeration to remove most of the moisture, and in addition there may be some desiccating material, such as soda lime or sodamide,⁸ following the cooler.

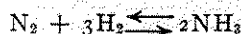
IV—SYNTHESIS OF AMMONIA

ADJUSTMENT OF COMPOSITION—The purified gas, consisting of about 3 parts hydrogen to 1 part nitrogen with 0.5 to 1.0 per cent of inert gases, such as argon and methane, passes into the ammonia circulating system. This is a separate and complete system wherein the entering gas acts as "make-up" to replace the gas synthesized and removed as ammonia. The uncombined gases after removal of ammonia repeat the cycle through the system together with the added "make-up." The supply of hydrogen and nitrogen to the circulating system should be in the average ratio of 3 : 1 to avoid the accumulation of the excess of either constituent. The chemical composition of the supply can evidently be best controlled by analysis of the gases in the circulating system where the cumulative effect of any slight inaccuracy of adjustment can be detected. The adjustment, if small, may be made by the injection of pure nitrogen or hydrogen obtained by liquefaction.¹⁶ It is well to run toward high hydrogen in the supply so that the adjustment may be entirely with nitrogen.

Methane and argon to the amount of 0.5 to 1.0

per cent in the entering gases are inert at the operating temperatures and, therefore, tend to accumulate in the circulating system, and some method of removal must be employed. The simplest method is to allow a fraction of the circulating gases to escape. A purge of gas equal to 10 per cent of the "make-up" gas would maintain a concentration in the circulating system of 5 to 10 per cent inert gases. This purge involves a loss of pure gas, while high concentrations of inert gas involve decreased ammonia reaction. Hence, the amount of purge and consequent inert concentration must be determined by a consideration of operating costs.

HEAT INTERCHANGE AND CATALYSIS—The reaction for ammonia synthesis is:



The extent to which this reaction progresses depends upon the equilibrium of the system, which is a function of the temperature, pressure, and relative concentrations of the constituents. As in carbon monoxide conversion the equilibrium is more favorable at lower temperatures, although the reaction velocity is greatly decreased. The equilibrium is, however, favorably altered and also the reaction velocity increased by a rise in pressure. The effect of comparatively large variations from the ratio of 3 hydrogen to 1 nitrogen is small, although the maximum ammonia concentrations and greatest reaction velocities are obtained with the theoretical mixture. Table X shows the equilibrium ammonia concentrations for the reaction in a 3 : 1 mixture.¹

TABLE X—EQUILIBRIUM NH₃ PER CENT

Temperature °C.	30 Atm. Per cent NH ₃	100 Atm. Per cent NH ₃	200 Atm. Per cent NH ₃
400	10.7	25.1	36.3
500	3.6	10.4	17.6
600	1.4	4.5	8.2
700	0.7	2.1	4.1

In the presence of a catalyst, reaction velocities are increased, so that a lower temperature with a more favorable equilibrium may be used. The equilibrium concentration of ammonia is not reached in practice. The activity of the catalyst will control the actual ammonia content, which seldom exceeds 5 per cent. The catalysts for this reaction as a class are very delicate chemically,¹⁷ and small amounts of carbon dioxide, oxygen, or moisture greatly decrease their activity, while carbon monoxide is also quite harmful. The catalysts are mainly of reduced iron with various promoters added.^{4,6,18}

With the present development of ammonia synthesis, temperatures of the order of 500° C. are employed. The reaction is exothermic to an extent sufficient to cause about a 15° C. temperature rise of the gases for each per cent of ammonia produced. The temperature gradient thus developed across the catalyst is available for maintaining heat interchange between exit and inlet gases through suitable apparatus. With proper design, sufficient heat interchange surface, and high conversion, the heat evolved in the reaction may offset all the heat losses. The supply of additional heat to the system is an important and serious problem.¹⁹

The construction of the apparatus in this portion

of the system is an important problem. At high temperatures and pressures, hydrogen diffuses through steel in addition to decarburizing the metal and causing dangerous changes in its physical properties. Ammonia also has a deleterious effect, due probably to a nitrification of the iron. Various alloy steels, combined with special design of the apparatus, obviate much of the difficulty.^{6,18,20}

REMOVAL OF AMMONIA AND CIRCULATION OF GAS—There are two distinct methods of ammonia removal:^{6,21} one by liquefaction, the other by absorption. When employing liquefaction, the gas containing the ammonia passes from the converter heat interchangers through cold interchangers and into the liquefaction coils,

TABLE XI—VAPOR PRESSURE OF LIQUID NH₃

Temperature °C.	NH ₃ Vapor Pressure Atm.	NH ₃ at 200 Atm. Per cent
0	4.2	2.1
-10	2.8	1.4
-20	1.83	0.91
-30	1.16	0.58
-40	0.68	0.34

externally and separately cooled by a refrigerating system. The ammonia gas is liquefied and may then be removed by mechanical separators or traps at the exit of the liquefiers, while the gas, still containing some residual ammonia, passes back through the cold interchangers and to the circulating pumps to repeat

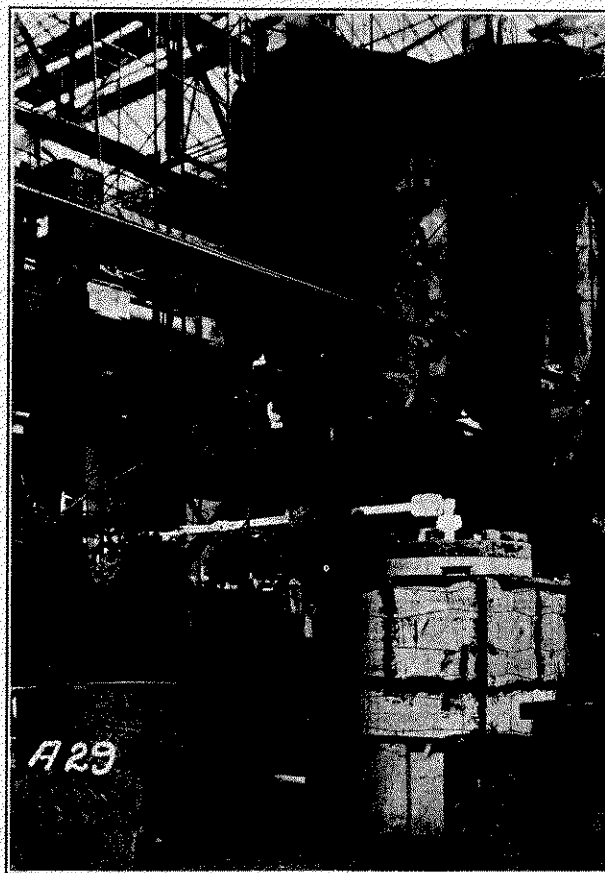


FIG. 6—AMMONIA LIQUEFIER WITH AUXILIARIES

its cycle. The amount of residual ammonia in the gas will depend on the temperatures reached in the liquefier (Table XI).²²

It is evident that very low temperatures are essential, especially with low ammonia conversion. Thus if 4 per cent ammonia is delivered by the catalyst at 100 atmospheres pressure with only -20°C . in the liquefier, nearly half the ammonia returns to the catalyst inlet. For the low temperatures necessary, special design and construction of the refrigerating system are required.

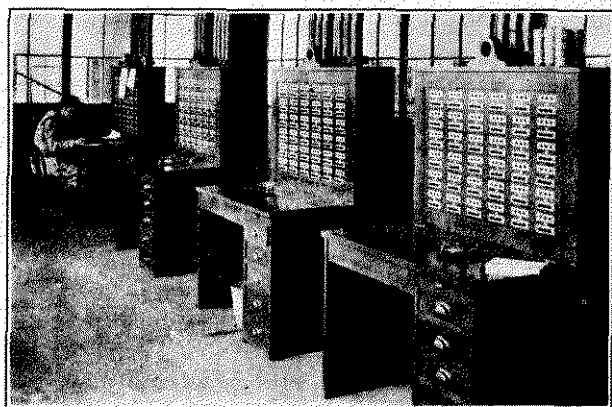


FIG. 7—PYROMETER CONTROL BOARDS

If absorption of the ammonia be the method of removal, the gas mixture, still under pressure, is scrubbed with water. This is best done in several stages with efficient cooling throughout, since the heat of solution is very considerable. The absorption apparatus may consist of scrubber towers similar to the cuprous scrubbers, or it may consist of water-cooled coils through which the gas and absorbing water are forced in intimate mixture. The water may be discharged with an ammonia concentration corresponding to commercial aqua ammonia, or even higher if desired. The uncombined gases are recirculated to the heat interchangers and converter. The gas will contain an appreciable quantity of water vapor which will hinder catalytic activity and this point must be well considered. The residual ammonia in the gas will be very low, depending on the temperature of absorption. Table XII gives the ammonia and water vapor pressures of 25 per cent aqua.²³

TABLE XII—VAPOR PRESSURES OF 25 PER CENT AQUA AMMONIA

Temperature C.	—Vapor Pressure—		—Vol. at 200 Atm.—	
	NH ₃ Atm.	H ₂ O Atm.	NH ₃ Per cent	H ₂ O Per cent
0	0.20	0.003	0.10	0.0015
+10	0.30	0.007	0.15	0.0035
+20	0.45	0.013	0.23	0.0065
+30	0.70	0.027	0.35	0.0135
+40	1.05	0.055	0.53	0.0275

Whichever method of ammonia removal is used, the quantity of gas to be circulated continuously per unit of ammonia extracted will be inversely proportional to the percentage of the gas removed as ammonia. The size of the system and design of piping, heat interchangers, ammonia removal installations, circulating pumps, etc., therefore, directly depend on the catalyst activity.

OPERATING QUANTITIES

Considering that gas, steam, water, and power are independently available, there follows an estimate of the quantities of these that will be necessary per short ton of ammonia for a Haber-Bosch process operating

at 100 atmospheres and delivering 10 tons of liquid anhydrous ammonia per day.

(1) Raw Gas (M cu. ft.)	
Water-Gas.....	85
Producer-Gas.....	45
Total	130
(2) Low Pressure Steam (tons)	
CO Converters.....	14
Cuprous Regeneration.....	1
Total	15
(3) Water (M cu. ft.)	
CO Converter Condensers.....	9
CO ₂ Scrubbers.....	7
Refrigerating Condensers.....	5
Additional.....	4
Total	25
(4) Power (k. w. h.)	
Main Compressors.....	1200
Water Scrubber Pumps.....	800
Refrigerating Compressors.....	400
Gas Circulating Compressors.....	200
Additional.....	400
Total	3000

SYNTHETIC AMMONIA PLANT AT SHEFFIELD, ALABAMA

The American pioneers in the direct synthesis of ammonia on a manufacturing scale were the General Chemical Company. They had been experimenting extensively on catalysts for the ammonia reaction and had made tentative designs for the construction of a commercial unit before the United States entered the World War. Pursuant to Section 124, "Nitrate Supply," of an Act of Congress, a committee was appointed²⁴ to determine the best, cheapest, and most available means for the production of nitrates or other nitrogenous materials. The committee investigated the direct synthetic ammonia process as it was being developed at that time by the General Chemical Company, and after consultation with that company they recommended the following action:²⁵

1—That the Government negotiate with the General Chemical Company for the right to use its synthetic ammonia process.

2—That contingent upon satisfactory result of such negotiations there be set aside from the \$20,000,000 appropriation such a sum, estimated at about \$3,000,000, as should be necessary to build a plant to produce by that process about 60,000 lbs. of ammonia per 24-hr. day.

In accordance with the above, arrangements were finally made whereby U. S. Nitrate Plant No. 1 was to be constructed according to the company's plans, but at government expense. The "National Defense Act" ruled that "the plant or plants provided for under this act shall be constructed and operated solely by the Government and not in conjunction with any other industry or enterprise carried on by private capital." Although construction and operation of the plant were by the Ordnance Department, U. S. A., the designs were furnished by the General Chemical Company, and construction as well as initial operation was carried out strictly under that company's supervision. Deviations in the process, modifications in apparatus, and changes in operating conditions were made only after consultation with, and approval of, the responsible engineers of the General Chemical Company stationed at the plant.

The total cost of Nitrate Plant No. 1 was about \$13,000,000, which cost covered that of the nitric acid plant, the concentrating plant, ammonium nitrate plant, and the permanent village for officers and employees. The expenditure was only partly from the funds allotted under the National Defense Act. There is chargeable to synthetic ammonia manufacture only about \$7,000,000 of the total. Perhaps an additional \$1,000,000 should be charged for completing parts of the plant and installation. Based on the rated capacity of 60,000 lbs. of ammonia daily, the investment would amount to nearly \$900 per annual ton of fixed nitrogen capacity.

The ammonia synthesis portions of the plant as installed consisted of three units, entirely independent of each other, not interconnected, but all under one roof. Unit No. 1, the only unit upon which operation was attempted, was rated at 15,000 lbs. of anhydrous ammonia per day. Unit No. 2 was a duplicate of No. 1, while Unit No. 3 was rated at 30,000 lbs. anhydrous ammonia per day. The total rated daily capacity of the plant was 30 tons of ammonia.

The process to be used was in general that discussed in the first part of this paper.²⁶ Operation was to be at 100 atmospheres pressure, or somewhat less, with ammonia removed by liquefaction. The raw gas mixture was to be made directly by the combined producer- and water-gas reactions. The carbon monoxide conversion was at atmospheric pressure with any necessary additional heat supply to be furnished by superheating the admixed steam, or by a free flame burning in the catalyst chamber. After condensation of the excess steam, compression to 100 atmospheres followed, which pressure was maintained through the rest of the system. The removal of carbon dioxide was to be accomplished in three stages, in series for the gas, with fresh water being supplied in parallel to each of the stages. The larger part of the carbon monoxide was to be removed by hot caustic solution, and the balance of that impurity by an ammoniacal cuprous carbonate solution. Final drying was accomplished by refrigeration followed by the use of desiccating material. In the circulating system additional heat was to be supplied to the gases entering the catalyst by a tubular heater similar to a steam superheater, and gas fired. The catalyst used was especially sensitive, being "composed of iron, sodium, and nitrogen."^{1,18} The ammonia formed was to be removed by liquefaction, refrigeration being supplied by a standard ammonia expansion installation, and the liquefied synthetic ammonia being discharged to storage tanks provided for that purpose.

At the start of operations many difficulties immediately developed, and changes in process and apparatus became necessary. Initial operation of the plant commenced in June 1918 and the first synthetic ammonia was produced in September. Continuous operation was, however, never realized, and the plant was definitely closed in January 1919, after having produced only a small amount of ammonia. The raw gas manufactured finally developed into a practically

straight blue water-gas, with most of the nitrogen added later as air for flame combustion in the carbon monoxide converter to maintain temperature there, while the overtaxed and inefficient steam superheaters were discarded. The compressors were quite satisfactory although under capacity when allowance was made for the hydrogen and nitrogen loss in the water scrubbers, in the inert gas purge, and in unavoidable leakage. The three water scrubbers operating with water in parallel gave much trouble and were inefficient in scrubbing and in water consumption, which difficulties were obviated by changing to a one-stage scrubbing. The removal of carbon monoxide with hot caustic involved many difficulties which were overcome only by the elimination of the caustic system with its towers, furnaces, pumps, etc. All the carbon monoxide was finally delivered to the cuprous solution for removal there. The cuprous system caused some difficulties and for improved absorption and efficiency reduced temperatures on both gas and solution were maintained. The purity of gas desired in view of the sensitiveness of the catalyst chosen was never obtained. In the circulating system the catalysis and heat interchange were not self-maintaining in temperature, and use of the high-pressure heating furnace installed for supplying additional heat was continually necessary, although it could not withstand the service for more than a few days at a time. Under-capacity of the refrigerating installation, excessive friction of gas circulation, and large unaccounted-for gas loss were some of the additional troubles in the circulating system. There were innumerable incidental mechanical difficulties with valves, with joints, with pressure gages, and with mechanical labor-saving devices. Experimenting and development stopped in January 1919, and negotiations looking toward an arrangement whereby the General Chemical Company should continue with this work for the Government were not successful.

As indicated above, many of the difficulties at U. S. Nitrate Plant No. 1 had been overcome by changes in the process or development of apparatus; many others can now be overcome in view of the past experience; and the balance can be overcome by additional experimenting and development. That final success can be hoped for is evident from the fact that in Germany there are two plants—one at Oppau with 100,000 tons of ammonia annual capacity, and one at Merckersburg with 200,000 tons rated capacity that were in regular operation during the war. The former was started just before the war, and extensive additions soon followed. The latter was built mainly during the war and three-fourths of the rated capacity was in operation before the armistice was signed.

The success of the German plants has shown that a process of this type may be successfully operated under war conditions. It has not yet been proved, although it seems probable, that it will be a commercial success under the post-war conditions that have arisen. All reports from Germany point to an optimistic feeling on the part of those connected with the industry there. No doubt the government has a very

considerable interest in the German plants,²⁷ and probably a large amount of the capital cost and all of the experimental cost has been written off as a war expenditure.

Conditions in America are somewhat less favorable for the private operation of a Haber-Bosch plant than in Germany because of higher labor costs and greater installation charges. The determining factors may depend on the development of methods of utilization of the ammonia and by-products, which in turn may involve combinations with other known processes. In the German plants the combination of the ammonia-soda with the direct synthetic ammonia process has been accomplished with much success. This combination may be of far-reaching importance in the development of direct synthetic ammonia manufacture. In the United States, during the past year, the Solvay Process Company and the General Chemical Company have together formed the "Atmospheric Nitrogen Corporation," capitalized at \$5,000,000, for the purpose of developing nitrogen fixation in this country. In Great Britain a corporation has been formed in which the Brunner-Mond Company (ammonia-soda process) is financially interested, and which has £5,000,000 available capital to design, build, and develop the direct synthetic ammonia process.

The situation with regard to private operation of a plant in this country does not apply to the government plant at Sheffield, Alabama, built as a war emergency measure. There the United States owns a complete plant designed to produce ammonia by a direct synthetic process. It had not reached an operative stage at the close of the war, and considerable alterations will have to be made before it can be considered operative. The Nitrate Division of the Ordnance Department, U. S. A., now has under way plans and redesigns for the modification of U. S. Nitrate Plant No. 1 to bring that plant to successful operation. This should by all means be done as a military preparedness measure. It will be recalled that Germany did not embark upon the World War until she had two independent nitrogen fixation processes—the cyanamide and the Haber—commercially developed. This country should not, after the lessons of the war, permit itself to be in a less favorable position than was Germany six years ago.

REFERENCES

- 1—F. Haber and R. LeRossignol, *Ber.*, **40** (1907), 2144; *Z. Elektrochem.*, **14** (1908), 181; *Ibid.*, **19** (1913), 53; F. Haber, *Chem.-Ztg.*, **34** (1910), 345; *Z. Elektrochem.*, **16** (1910), 244; F. Haber, *et al.*, *Ibid.*, **20** (1914), 597; *Ibid.*, **21** (1915), 191.
- 2—Haber, D. R. P. 229,126 (1909); 238,450 (1909); Haber and Le-Rossignol, U. S. Patents 971,501 (1910); 999,025 (1911); 1,006,206 (1911); 1,202,995 (1916); Badische Anilin und Soda Fabrik, D. R. P. 235,421 (1908); 259,996 (1911).
- 3—B. A. S. F. (C. Bosch), U. S. Patent 1,102,716 (1914); Brit. Patent 26,770 (1912); Fr. Patent 459,918 (1913); General Chemical Co. (deJahn), Brit. Patent 124,760 (1918).
- 4—H. C. Greenwood, "Industrial Gases," (Ballière, Tindall & Cox, 1920).
- 5—B. A. S. F., Brit. Patent 27,117 (1912); (C. Bosch) U. S. Patent 1,115,776 (1914); (C. Bosch) U. S. Patent 1,200,805 (1916).
- 6—General Chemical Co. (deJahn), Brit. Patent 120,546 (1918).
- 7—Vignon, Fr. Patent 389,671 (1908); B. A. S. F., D. R. P. 282,505 (1913); Brit. Patents 8,030 (1914); 9,271 (1914); U. S. Patent 1,196,101 (1916); D. R. P. 289,106 (1914); General Chemical Co. (deJahn), Brit. Patent 120,546 (1918).
- 8—Harries, *J. Gasbel.*, **1894**, 82; Luggin, *Ibid.*, **1898**, 713; Boudouard, *Ann. chim. phys.*, **24** (1901), 1; Hahn, *Z. physik. Chem.*, **44** (1900), 510; *Ibid.*, **48** (1904), 735; Farup, *Ibid.*, **50** (1906), 276; Meyer and Jacobi, *J. Gasbel.*, **82** (1909), 282, 305; Clement, Bureau of Mines, *Bulletin* **7** (1911); Haber, "Thermodynamics of Technical Gas-Reactions" (Longmans, Green & Co., 1908).
- 9—B. A. S. F., Brit. Patent 27,955 (1912); D. R. P. 292,615 (1912); D. R. P. 293,943 (1913); Fr. Patent 469,907 (1913); Brit. Patent 16,494.
- 10—Lane, Brit. Patent 11,878 (1910); General Chemical Co. (deJahn), Brit. Patent 124,761 (1918); Greenwood, "Industrial Gases."
- 11—Société l'Air Liquide, Brit. Patent 15,053 (1914).
- 12—Wroblewski, *Compt. rend.*, **94** (1882), 1355; Bohr and Bock, *Wied. Ann. Phys.* [2], **44** (1891), 318.
- 13—C. Bosch, *Z. Electrochem.*, **24** (1918), 361.
- 14—B. A. S. F., Brit. Patent 1,759 (1912); U. S. Patents 1,126,371 (1915); 1,333,087 (1915); D. R. P. 254,043 (1911); D. R. P. 279,954 (1913).
- 15—F. A. Weber, "The Action of Carbon Monoxide on Caustic Soda," Dissertation, Karlsruhe, **1908**; G. R. Fonda, "The Action of Carbon Monoxide on Alkalies," Dissertation, Karlsruhe, **1910**.
- 16—B. A. S. F., D. R. P. 265,295 (1912); 1,075,085 (1913).
- 17—Greenwood, *Loc. cit.*, Patents by deJahn, Haber and LeRossignol, Bosch and Mittasch.
- 18—General Chemical Co. (deJahn), U. S. Patents 1,141,947 (1915); 1,143,366 (1915).
- 19—B. A. S. F., D. R. P. 259,870 (1911); 268,929 (1912).
- 20—B. A. S. F., D. R. P. 254,571 (1911); D. R. P. 256,296 (1911); D. R. P. 275,156 (1911); U. S. Patent 1,188,530 (1916).
- 21—B. A. S. F., D. R. P. 235,421 (1908); D. R. P. 259,996 (1911); D. R. P. 270,192 (1912); U. S. Patent 1,202,995 (1916).
- 22—G. A. Goodenough, "Properties of Steam and Ammonia" (J. Wiley & Sons, Inc., 1915).
- 23—Perman, *J. Chem. Soc.*, **83** (1903), 1169; M. J. Eichhorn, in "Ice and Refrigeration," Chicago (August 1918).
- 24—"National Defense Act," approved June 3, 1916, Public Document, War Department, *Bulletin* **16**, June 22, 1916.
- 25—"Statement of Action Taken and Contemplated Looking to the Fixation of Nitrogen," by Division T, Ordnance Office, War Department, Aug. 21, 1917, *This Journal*, **9** (1917), 829.
- 26—General Chemical Co. (deJahn), Brit. Patents 120,546 (1918); 124,760-1-2 (1918).
- 27—N. Caro, *Chem. Ind.*, **42** (1919), 877.

GASOLINE FROM NATURAL GAS. III—HEATING VALUE, SPECIFIC GRAVITY, AND SPECIFIC HEAT

By R. P. Anderson

UNITED NATURAL GAS COMPANY, OIL CITY, PENNSYLVANIA

Received May 12, 1920

The present paper of this series on natural-gas gasoline problems is devoted to a discussion of the following topics:

- (1) Relationship between heating value and number of carbon atoms per molecule of hydrocarbon.
- (2) Relationship between heating value and specific gravity of gasoline.
- (3) Effect of removing gasoline upon heating value and specific gravity of natural gas.
- (4) Specific heat of natural gas and gasoline vapor.

(1) RELATIONSHIP BETWEEN HEATING VALUE AND NUMBER OF CARBON ATOMS PER MOLECULE

If the assumption be made that the relationship between the heating value of normal paraffin hydrocarbons, expressed in calories per gram-molecule, and the number of carbon atoms per molecule is a linear one, it becomes a simple matter to compute tables of heating values that are valuable in the natural-gas gasoline industry. Such computations have been made for the heating values per lb., per gal., and per cu. ft. of vapor of the normal paraffin hydrocarbons, pentane to undecane, inclusive, and the results are incorporated in Table I. Thomsen's figures for the heating value of methane, ethane, and propane form the basis of the table and have been included in it.